

FORM PTO-1300 (Modified)
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES

27153.2400

DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

CONCERNING A FILING UNDER 35 U.S.C. 371

09/868283

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP99/10036

17 December 1999

18 December 1998

TITLE OF INVENTION

METHOD FOR DARKENING A SUPERFICIAL LAYER WHICH
CONTAINS ZINC AND WHICH IS OF A MATERIAL PIECE

APPLICANT(S) FOR DO/EO/US

KRUSE, Thomas

MEISTERJAHN, Peter

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
- ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- ☒ A copy of the International Search Report (PCT/ISA/210)
- ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
- ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
- ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
- ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

1) Power of Attorney and Designation of Domestic Representative

2) Statement Claiming Small Entity Status Under 37 C.F.R. 1.9(f) and 1.27(c) - Small Business Concern

3) Receipt Postcard

U.S. APPLICATION NO. (UNKNOWN), SEE 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

097868285

PCT/EP99/10036

27153.2400

21. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). ☐ 20 ☐ 30

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	28 - 20 =	8	x \$18.00	\$144.00
Independent claims	2 - 3 =	0	x \$78.00	\$0.00

Multiple Dependent Claims (check if applicable). ☐

TOTAL OF ABOVE CALCULATIONS	=	\$1,004.00
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Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☒

SUBTOTAL	=	\$502.00
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Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). ☐ 20 ☐ 30

TOTAL NATIONAL FEE	=	\$502.00
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☒

TOTAL FEES ENCLOSED	=	\$542.00
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Amount to be:	\$
refunded	
charged	

☒ A check in the amount of **\$542.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. **19-2814** in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **19-2814** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Damon L. Boyd
Snell & Wilmer L.L.P.
One Arizona Center
400 East Van Buren
Phoenix, Arizona 85004-2202

SIGNATURE

Damon L. Boyd

NAME

44,552

REGISTRATION NUMBER

15 June 2001

DATE

IN THE UNITED STATES PATENT
AND TRADEMARK OFFICE

DESIGN PATENT

Applicant:	Kruse et al.	Docket No.:	27153.2400
Serial No.:	To Be Assigned	Art Unit:	To Be Assigned
Filed:		Examiner:	Not Yet Assigned
Title:	METHOD FOR DARKENING A SUPERFICIAL LAYER WHICH CONTAINS ZINC AND WHICH IS OF A MATERIAL PIECE		

PRELIMINARY AMENDMENT

BOX PCT

Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Prior to examination, please amend the subject application as follows.

IN THE CLAIMS

5. (Amended) Process according to [one of the Claims] Claim 3 [or 4,] characterized by being carried out at a pH value exceeding 13.

6. (Amended) Process according to [one of the Claims from] Claim 3 [to 5,] characterized by anodic oxidation being executed during a period of treatment (t) of between 1 second to 10 minutes.

8. (Amended) Process according to [one of the Claims] Claim 3 [to 7,] characterized by being carried out with direct voltage.

11. (Amended) Process according to [one of the Claims from] Claim 8 [to 10,] characterized by the dipping bath containing from 25 to 35 g/l NaOH and from 30 to 50 g/l NaNO_3 or $\text{Na}_2\text{B}_4\text{O}_7$.

13. (Amended) Process according to [one of the claims from] Claim 3 [to 7,] characterized by being carried out with alternating voltage.

15. (Amended) Process according to Claim 13 [or 14,] characterized by the dipping bath containing from 10 to 35 g/l NaOH and from 30 to 60 g/l NaNO_3 or $\text{Na}_2\text{B}_4\text{O}_7$.

17. (Amended) Process according to [one of the Claims] Claim 13 [to 16,] characterized by the dipping bath containing from 10 to 15 g/l of NaOH and from 10 to 60 g/l of an alkali salt being selected from among the group comprising phosphates, acetates, carbonates, sulphates, oxalates, citrates, and borates of alkali metals.

18. (Amended) Process according to [one of the Claims] Claim 1 [to 17,] characterized by the piece of material being subjected to a dipping treatment in an acid prior to anodic oxidation.

IN THE SPECIFICATION

On Page 1, please delete the paragraph beginning "The quoted paper only mentions rough and wide ..."

and insert

-- The quoted paper only mentions rough and wide ranges of parameter for the treatment process, not indicating any details, however, of homogeneity and uniformity of the darkened surfaces. --

REMARKS

The Examiner is invited to telephone the undersigned at (602) 382-6337 at the Examiner's convenience, if that would help further prosecution of the subject application. Applicants authorize and respectfully request that any deficiency in fees be debited from deposit account no. 19-2814, **for which purpose a duplicate copy of this sheet is attached. This statement does NOT authorize charge of the Issue Fee.**

Respectfully submitted,

Date: 15 June 2001

By: 

Damon L. Boyd, Reg. No. 44,552

Snell & Wilmer L.L.P.
One Arizona Center
400 East Van Buren
Phoenix, AZ 85004-2202
Phone: (602) 382-6337

IN THE UNITED STATES PATENT AND
TRADEMARK OFFICE

PATENT

Applicant(s) or
Patentee(s):

Docket No.: 27153.2400

Serial or Patent
No.:

Group Art Unit:

Filed or Issued:

Examiner:

TITLE: Method For Darkening A Superficial Layer Which
Contains Zinc And Which Is Of A Material Piece

**STATEMENT (DECLARATION) CLAIMING
SMALL ENTITY STATUS UNDER 37 C.F.R. §§1.9(f) AND 1.27(c) --
SMALL BUSINESS CONCERN**

Assistant Commissioner of Patents
Washington, D.C. 20231-9998

Sir:

I hereby state that I am:

[] the owner of the small business concern identified below.

[x] an official of the small business concern empowered to act on behalf of the concern identified below.

NAME OF CONCERN: Ewald Dörken AG

ADDRESS OF CONCERN: Wetterstr. 58, 58313 Herdecke, Germany

I hereby state that the above identified small business concern qualifies as a small business concern as defined in 13 C.F.R. §§121.3-18, and reproduced in 37 C.F.R. §1.9(d), for purposes of paying reduced fees under Section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby state that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled:

Method For Darkening A Superficial Layer Which Contains Zinc
And Which Is Of A Material Piece

by inventor(s) Thomas Kruse, Prof. Dr. Peter Meisterjahn

described in:

Snell & Wilmer LLP
One Arizona Center
400 East Van Buren
Phoenix, Arizona 85004-0001
Tel: (602) 382-6000
Fax: (602) 382-6070

[x] the specification filed herewith
[] application serial no. _____, filed _____
[] patent no. _____, issued _____

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who would not qualify as a small business concern under 37 C.F.R. §1.9(d) or a nonprofit organization under 37 C.F.R. §1.9(e).

NOTE: Separate statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 C.F.R. §1.27)

NAME: _____

ADDRESS: _____

[] Individual [] Small Business Concern [] Nonprofit Organization

NAME: _____

ADDRESS: _____

[] Individual [] Small Business Concern [] Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 C.F.R. §1.28(b))

NAME OF PERSON SIGNING: Dr. Jochen Plaßmann

TITLE OF PERSON OTHER THAN OWNER: Managing Director

ADDRESS OF PERSON SIGNING: Wetterstr. 58, 58313 Herdecke, Germany

SIGNATURE:  DATE 5.6.01

*Translation from the German Language***Method for the darkening of a surface layer of a piece of material containing zinc**

The invention comprises a method for the darkening of a surface layer of a piece of material containing zinc during which the piece of material is oxidized in a dip bath which contains a hydrous solution of a hydroxide and a nitrate, a piece of material treated by such a method, and also the electrolytes for the realization of the method and the methods for pretreatment of the pieces of material.

Generally, for the darkening of material surfaces containing zinc, the method known as "blackening by chromating" has been used so far. This method uses the highly reactive molecule of Cr_6 which is, however, according to the most recent findings, strongly detrimental to health.

A less harmful method for the darkening of pure zinc surfaces is described in the scientific paper "production of a protective and decorative coating on zinc by alternating-current treatment at 50 Hz in alkaline solutions" by M. Al. Encheva, published in the J. Appl. Chem. of the USSR 45.318 (1972). In this paper, a dip bath for the darkening of surfaces made of zinc is presented which contains as an electrolyte, within the scope of anodic oxidation, hydrous solutions of NaOH and NaNO_3 . This scientific paper is focussed both on the improvement of corrosion resistance of pieces of material with a zinc-coated surface, and on the appearance of the surface-treated pieces of material, especially their transformation.

The quoted paper only mentions rough and wide... [Text missing. Translator's remark]

16.11.2000

EP 009910036

- 2 -

not indicating any details, however, of homogeneity and uniformity of the darkened surfaces. A further development of the familiar method is described, regarding its application on solar collectors, in the published study "Optimization and Microstructural Analysis of Black-Zinc-Coated Aluminium Solar Collector Coatings" by S. N. Patei et al., published in "Thin Solid Films", 113 (1984), p. 47).

In EP 0 339 578 A1, a process for the production of black-coated steel strips is described which consists of an electrolyte treatment in a dipping bath containing from 75 to 200 g/l of a compound selected from among the group comprising hydroxides, sulphates and chlorides of sodium, potassium or nickel. Preferably, the dip bath contains nitrate ions in a quantity from 2 to 100 g/l. For the anodic oxidation used for this process, current densities within the range from 30 to 200 A/cm² are used. This process is preferably operated with alternating current. The dipping bath must absolutely contain both an inhibitor substance and a complex-forming one.

FR 2758339 A describes a method for anti-corrosion treatment of metallic workpieces, in particular ferruginous ones. The dip bath used for electrolysis contains between 300 to 700 g/l of alkali hydroxides, between 20 and 50 g/l alkali nitrates and/or nitrites, between 40 to 100 g/l borax, and between 10 to 40 g/l tensides, the dipping bath being maintained at a temperature within the range from 110 to 130°C.

The scientific paper by Fry H.E.A. with the title "The Anodic Oxidation of Zinc and a Method of Altering the Characteristics of the Anodic Films", published in "Journal of the Electrochemical Society", volume 106, No. 7, July 1959, pages...

REVISED PAGE

...606-611, equally describes methods of anodic oxidation of zinc. Black coatings have been achieved by anodizing zinc in a sodium hydroxide solution with a current density of about 200 mA/cm². Dark layers were apparent in case of dip bath solutions containing sodium carbonate and sodium hydroxide, if low anode potentials were used. All samples were immersed into the bath for 15 seconds without voltage and prior to feeding the potential.

From this starting point, the invention is based on the purpose to develop processes for the darkening of a surface layer of a piece of material containing zinc in such a way that all treated surfaces show increased homogeneity, adhesion and uniformity, and also to provide the respective piece of material having such properties, and also the electrolytes for the execution of such processes.

The requirement is met by a method according to Claim 1. The dip bath solution preferably contains an alkali salt or ammonium salt from among the group comprising phosphates, acetates, carbonates, sulphates, exalates, citrates and borates of alkali metals or ammonium.

If these process parameters are maintained, the result is the homogenous darkening of the surface layers of the surfaces of those pieces of material which contain zinc from a dark gray colour to black, leading also to an excellent homogeneity of the surface layer. It should be emphasized that it is a comparatively low current density which will lead to the desired colour changes of the surface layers, quite contrary to the method described in the scientific paper.

The method is characterized by the piece of material being immersed into the dip bath of a device which is equipped with, at least, two electrodes for anodic oxidation, the alternating or direct voltage being fed to the electrodes prior to immersion of the piece of material into the bath, and only then the piece of material will be immersed into the bath while maintaining the voltage which should initially be 8 volts for alternating current and initially 20 volts for direct current with an electrode spacing of 3 cm. When the piece of material is immersed, first a high current will flow between the electrodes. After the expiry of a period of a few seconds after immersion of the piece of material, the current density required for this method should be adjusted by reducing the voltage. Such a method will essentially contribute to the homogeneity of the darkened surface layer. It is important to provide of a minimum current flowing during immersion of the piece of material for the purpose of improvement of homogeneity.

REVISED PAGE

Appropriate pieces of material could be all suitable substrates which are coated with a zinc layer whose surface has been treated, and also pure zinc. Instead of pure zinc, you could use a zinc alloy presenting, in relation to the dry layer, a high content of zinc, e.g. a minimum of 50 percent in weight. Additionally, it is possible to apply a pure zinc layer, or a zinc alloy layer by any other method to a substrate, such as vapor deposition processes like PVD and CVD, hot dip galvanizing and all methods for mechanical surfacing of such layers. In individual cases, mat zinc-coated or bright galvanized steel sheets may be used. Possible zinc alloys may be, among others, Zn/Fe, Zn/Ni, Zn/Fe/Co, Zn/Co, Zn/Al, Zn/Sn, Zn/Mn.

Titanium may be used as the opposite electrode for the piece of material to be treated. Other materials could also be used for the electrodes if the required current density is adapted accordingly. Other possible materials for the opposite electrode are precious metals, stainless steel, tantalum, graphite.

The pH value should preferably be adjusted by means of the respective concentration of NaOH or KOH. The pH value will be finally decisive, while, for providing the OH⁻ groups, it is also possible to use amines or other organic bases, soluble potassiums (sodium silicates, potassium silicates, lithium polysilicates), amino hydrosilicones, basified titanate acid esters (silica esters) in single or combined form. Optionally, zirconium compounds which are made available/resembling? (for) groups similar to OH⁻ may be used [Sense? Translator's remark].

For acceleration of the treatment process, the pH value should be higher than 13. This is also applicable for all methods relating to the invention which are described later on. In this case,...

...anodic oxidation may be processed over a treatment period of from 1 second to 10 minutes until the surface layer has darkened.

The method can optionally be carried out with direct voltage or alternating voltage. Generally, for operation with direct current, lower current densities will be required for achieving darkening of the surface layer.

When operating the process with direct voltage, the temperature of the bath may be within the range from 15 to 45°C, while the current density is within the range from 0.003 to 0.15 A/cm². Working with direct voltage has the advantage of good results of surface layer darkening being obtained even at room temperature and with very low current density.

Alternately, the bath temperature may be equal to from 35 to 45°C when operating the process with alternating voltage, while the current density is within the range from 0.1 to 0.15 A/cm².

Recommendations about temperatures and composition of the dip bath for anodic oxidation with direct or alternating current are indicated in the claims.

The process described above may also be supplemented by pretreatment steps, where any structural non-homogeneities of the surfaces of the piece of material or high organic parts can be accounted for. In both cases, the piece of material is subjected to a dip treatment (activating/decoupling) in some acid, prior to anodic oxidation.

For the removal of any visible structural non-homogeneities, you can use, as an acid, H_2SO_4 which is at least 0.5 molar, carrying out the dipping treatment over a period of a minimum of 10 seconds. The period of treatment will depend on the visible impression presented by the surface layer on visual inspection.

Particularly when a high portion of organic parts is contained in the surface layer, you can use as an acid 2 molar H_2SO_4 for a pretreatment step. Afterwards you can temper the piece of material at a temperature of about 200°C , the period of such a pretreatment being in the range of 1 hour.

All of the pretreatment steps described above are particularly suitable with pieces of material whose surface layer is made of bright zinc. The brighteners used for the production of bright zinc may be responsible for a high organic portion in the surface so that no sufficiently darkened appearance of the surface layer will be achieved.

After anodic oxidation, the quality of the appearance of the surface layer may be improved by an after-treatment step where the piece of material is also exposed to acid in a dipping process. Such a secondary treatment may, for instance, be related to the presence of iridescent films on the darkened surface layer which deteriorate the optical impression of the surface layer.

For the prevention of such iridescent films, in particular, the piece of material may be dipped into a 10 percentage CH_3COOH , maintaining the dipping over a period of at least 30 seconds. Good results have been achieved with...

...a period of one minute for the dipping treatment.

A bipolar method is also possible, both electrodes for anodic oxidation being formed by a piece of material whose surface contains zinc, i.e. the opposite electrode being equally present as a piece of material whose surface is to undergo treatment as well. This will about double the production rate achieved for pieces of material with darkened surfaces.

When pieces of material are surface-treated which have been galvanized with pure zinc, an average thickness of a minimum of $8\text{ }\mu\text{m}$ of the contact surface layer may be of advantage. This relates, in particular, to such pieces of material which form the components of a frame. Such frame components will have edges whose surface treatment may be difficult. The mentioned average contact surface thickness will help to maintain corrosion resistance, in particular.

Particularly good results for darkening the surface layer of pieces of material can be achieved if the surface layer contains at least 50 percent in weight of zinc.

Another object of the invention includes a piece of material which is produced with the processes described above and surface treated. The zinc-containing surface is characterized by its transformation in structure by anodic oxidation in such a way that the result will be a very high absorption capacity, for instance, in the visible spectral region, thus making the surface seem blackened. The thickness of the transformed part of surface layer of the piece of material is within the range of between several μm and several $100\text{ }\mu\text{m}$, preferably between approx. 5 to $500\text{ }\mu\text{m}$.

...μm. A very low degree of reflection can be adjusted, especially for infrared radiation. Moreover, the transformed surface layer is characterized by adhesion in itself and to the adjacent material providing therefore a good solidity.

The provision of the OH⁻ groups can preferably be adjusted by a respective concentration of NaOH or KOH. The electrolyte may also contain additives for antifoaming, for the improvement of subsurface wetting or corrosion inhibitors in solid or liquid consistency in a concentration of 0.01- 100 g/l. Suitable organic solvent additives will be glycols, glycol ether, glycol ether ester, and alcohols of any kind according to their use, which may be present by themselves or in concentration with each other.

Included as another object of the invention is a process for the darkening of a surface layer of a piece of material containing zinc, the material being subjected to a treatment in a dipping without the use of electrolytic effects, the dip bath containing a hydrous solution of a hydroxide and a nitrate, the hydrous solution having...

...a pH value within the range from 8 to 14 and a concentration of NH_4NO_3 or NaNO_3 within the range from 40 to 50 g/l, the dipping being carried out at a temperature within the range from 15 to 45°C.

When carrying out the last-mentioned process, the pH value of the dip bath should be higher than 13, the bath temperature should be within the range from 15 to 25°C, and the period of treatment should not fall below 10 seconds. If you use, for instance, an electrolyte containing NaOH in a concentration of 30 g/l, and NaNO_3 in a concentration of 40 g/l, the process being carried out at room temperature, darkening of the ZnFe surface layer is obtained as early as after 20 to 30 seconds. The iron portion on the ZnFe will be, for instance, within the range from 0.3 to 1.5 percent in weight.

The above-mentioned specified task is equally fulfilled by a process for the darkening of a surface layer of a piece of material containing zinc, during which the piece of material is subjected to anodic oxidation in a dip bath containing a hydrous solution of a hydroxide, where

- the dipping bath has a pH value within the range from 8 to 14,
- the process is carried out with direct current at a current density of within the range from 2 to 30 mA/cm², and
- the piece of material is immersed into the dipping bath at the beginning of anodic oxidation when voltage has already been fed.

It could be observed that, when the current density is lower than...

...2 mA/cm² no darkening will occur, while, when 30 mA/cm² are exceeded, at first darkening will occur, but the relevant layer will then dissolve again within a few seconds. Preferably an alkali hydroxide should be used whose pH value should be higher than 13.

The provided methods and the pieces of material produced by these processes offer the following benefits: the use of harmful Cr₆ can be avoided; the compatibility with commercial galvanizing techniques is ensured (like, for instance, aluminium anodizing methods), and therefore well-known plant engineering (frame-type or barrel-type methods) including the associated know-how can be used to a large extent; and, in case you intend to overpaint the piece of material with, for instance, a transparent, dark, or black, if any, paint system on the basis of organic or inorganic binders, the contrast difference of the paint layer to the transformed surface of the piece of material is low so that low expenditure of material is required for reaching hiding capacity for the surface of the piece of material.

Some typical design examples of the processes included in the invention and the pieces of material treated according to these are explained in the following for better comprehension of the invention.

On the examples of design explained below, the piece of material each used will be a bright galvanized steel sheet. If not otherwise stated, the steel sheet is dipped into the respective dipping bath when voltage is applied to it.

Example 1)

The first processing step for surface treatment of the piece of material is its immersion into 0.5 M H₂SO₄ for about one minute. This step of the process is used for...

...improving homogeneity of the surface to be treated later on in a process of anodic oxidation and will be required only if the material surface to be treated presents unusual non-homogeneities.

In a second process step, anodic oxidation of the piece of material is carried out (electrode spacing: 3 cm; a few volts of alternating voltage), all opposite electrodes being made of titanium sheet. For anodic oxidation, a dip bath is being used which is characterized by a hydrous solution of NaOH and NaNO_3 as an electrolyte, the selection of concentrations being the following: 30 g/l of NaOH and 40 g/l of NaNO_3 . The bath temperature T is 40°C , while the current density i is equal to 0.1 A/cm^2 . The treatment period is within the range from 2 to 10 minutes.

For anodic oxidation in this example of design, the piece of material will form the collector electrode of an alternating current circuit which is operated with 50 Hz alternating current, while the titanium sheet acts as the opposite electrode.

In a third process step, the piece of material is removed from the dip bath for anodic oxidation, cleaned in a flushing process which may consist of multiple stages, if any, and dried finally.

The process of anodic oxidation will transform the surface layer of the piece of material in order to result in a homogeneous structure and a uniformly darkened surface layer colour. The thickness of the transformed part of surface layer will depend in the first place from the treatment period t and will be within the range of several 10 to several 100 nm. The transformed surface layer provides self-adhesion in itself and firm adhesion to the surface of the non-transformed...

...zinc.

Example 2)

The second process step may also be carried out with the following parameters, keeping to the above-mentioned treatment period t , the titanium sheet opposite electrode and the bath temperature T : electrolyte composition 13 g/l NaOH and 50 g/l in water; current density i 0.05 A/cm². The result are pieces of material with transformed surface, their properties being equal to those which have been explained with Example 1) for the second process step.

Both of the described examples of execution for the second process step are contained within a limiting range for the process parameters of NaOH concentration, NaNO₃ concentration, and current density. These parameters may be changed within the limits described above, the surface layer quality being maintained to a substantial extent.

The bath temperature T and treatment period t may be altered according to each application, as well.

Example 3)

While using the same second process step as described in examples 1) and 2), the first process step will be modified in such a way as to remove any disturbingly high organic parts from bright galvanizing of the steel sheet.

For this purpose, the first process step will consist of a dipping process into 2 M H₂SO₄ for more than 10 seconds, for example for up to 2 minutes. The first process step will also comprise the tempering of the piece of material at about 200°C. The tempering step lasts for about 1 hour.

Example 4)

This example accounts for the fact that, although the process steps are carried out as explained above and according to examples 1) to 3), it may be possible that, after anodic oxidation, iridescent films occur on material surface, especially in the case of bright galvanized steel sheet.

To avoid such iridescent films, the piece of material is subjected to a dipping treatment in 10 percentage CH_3COOH over a period of at least 3 seconds.

Example 5)

Contrary to Example 1), this example shows a process carried out with direct voltage. The piece of material will again be a bright galvanized steel sheet.

Process parameters include the following: Electrolyte: 30 g/l of NaOH, 40 g/l NaNO_3 in water. Direct current density is 0.017 A/cm^2 , while the period of treatment takes 5 minutes.

Bath temperature is equal to room temperature.

This example will have the particular advantage that lower current density, as compared to alternating voltage, can be used for the process. Moreover, the formation of hydrogen which will be produced in the cathodic half-wave when processing with direct voltage, can be totally avoided when using direct voltage for the process. Hydrogen may lead to an embrittlement of the surface layer of the piece of material.

The following example makes evident how to achieve the darkening of a surface layer of a piece of material without electrolytic effects.

Example 6)

This example has been carried out on a piece of material with a surface layer made of ZnFe, where the part of iron is within the range from 0.5 to 1.5 percent in weight.

The process is carried out without current at room temperature, the electrolyte containing 30 g/l of NaOH and 40 g/l of NaNO_3 .

After 20 to 30 seconds of dipping, darkening of the surface layer will occur on the piece of material.

Example 7)

Contrary to the examples described above, for this process, a second piece of material is used as the opposite electrode, which substantially has the same structure as the piece of material to be processed, thus facilitating bipolar operation. Both pieces of material will be treated simultaneously, resulting, as above, in darkened surface layers when alternating voltage is fed.

Example 8)

With a pH value within the range from 13.4 to 13.6, zinc layers which have been applied by galvanization, are anodized when alternating current within the range from 0.1 to 0.15 A/cm^2 is applied. For the following sodium salts, a darkening of surface providing good homogeneity has been observed: sodium phosphate (10-40 g/l), sodium acetate (10-40 g/l), sodium carbonate (10 g/l), sodium sulphate (10-40 g/l), sodium oxalate (10-40 g/l), sodium citrate (10-40 g/l), and sodium borate (10-40 g/l).

It is totally conceivable to use salt concentrations of up to 60 g/l, at least.

With sodium borate, a minimum current density of 0.05 A/cm^2 is sufficient for blackening the surfaces.

Example 9)

At a pH value within the range from 13.8 to 13.95, the darkening of surfaces containing zinc is possible if the same values of current and salt concentration as in the previous example are used. With both sodium nitrate and sodium borate, surface blackening can be observed. All other alkali salts mentioned in the previous example will lead to a dark gray colour change.

Regarding the execution of anodic oxidation with alternating voltage, the two examples mentioned last show a difference regarding the salts used for achieving a satisfactory degree of darkening. The difference is related to NaOH concentration. If you use NaOH concentrations within the range from 10 to 15 g/l, other salts with good darkening results, besides sodium nitrate and sodium borate, can be used, such as phosphates, acetates, carbonates, sulphates, oxalates, citrates of alkali metals or ammonium. The best results of darkening can be achieved with the salts sodium nitrate and sodium borate, when compared to this, if the NaOH concentration range exceeds 30 g/l.

The dipping bath may also contain several salts without the darkening result being deteriorated, for instance, a mixture of sodium nitrate and sodium borate.

Example 10)

If the pH value is within the range from 13.4 to 13.6, surfaces containing zinc were anodized with direct current. Darkening, or even blackening, with a good surface homogeneity has already been observed at current densities within the range from 3×10^{-4} to 20×10^{-3} A/cm², depending of the salt used each time. In particular, when using sodium borate and sodium nitrate, black surfaces with good homogeneity...

...can be obtained.

Concerning the execution of anodic oxidation with direct current, far better results can be achieved with the salts sodium nitrate and sodium borate than with any other alkali or ammonium salts.

Example 11)

It is, however, quite possible to achieve darkening of a surface containing a minimum of 50% zinc by using pure NaOH. A hydrous solution with 30 g/l NaOH and a current density of 15 mA/cm² direct current, anodic oxidation will lead to surface darkening.

Therefore, the salts studied in the previous examples seem, in the first place, to increase the current density interval for the darkening of a surface layer containing zinc.

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Patent Claims

1. Process for the darkening of a surface layer of a piece of material containing zinc, for the purpose of anodic oxidation of the piece of material in a dipping bath which contains a hydrous solution of a hydroxide, characterized by
 - the dipping bath having a pH value within the range from 8 to 14,
 - the dipping bath temperature (T) being within the range from 15 to 45°C,
 - the current density (i) for anodic oxidation being within the range from 3×10^{-4} to 0.5 A/cm²,
 - the piece of material being dipped into the bath at the beginning of anodic oxidation when voltage has already been fed.
2. Process according to Claim 1, characterized by
 - the process being carried out with direct current with a current density within the range from 2 to 30 mA/cm².
3. Process according to Claim 1, characterized by
 - the dip bath solution containing an alkali or ammonium salt,
 - the concentration of alkali or ammonium salt being within the range from 10 to 60 g/l, and...

- the alkali or ammonium salt being selected from among the group comprising phosphates, acetates, carbonates, sulphates, oxalates, citrates, and borates of alkali metals or ammonium.
- 4. Process according to Claim 3, characterized by the pH value being set by means of an adequate concentration of NaOH or KOH.
- 5. Process according to one of the Claims 3 or 4, characterized by being carried out at a pH value exceeding 13.
- 6. Process according to one of the Claims from 3 to 5, characterized by anodic oxidation being executed during a period of treatment (t) of between 1 second to 10 minutes.
- 7. Process according to Claim 6, characterized by anodic oxidation being executed over a period of treatment (t) of between 30 seconds to 3 minutes.
- 8. Process according to one of the Claims from 3 to 7, characterized by being carried out with direct voltage.
- 9. Process according to Claim 8, characterized by the dipping bath temperature being within the range from 15 to 30°C, and the current density (i) being within the range from 3×10^{-4} to 0.15 A/cm².
- 10. Process according to Claim 9, characterized by the current density (i) being within the range from 0.3 to 20 A/cm².
- 11. Process according to one of the Claims from 8 to 10, characterized...

...by the dipping bath containing from 25 to 35 g/l NaOH and from 30 to 50 g/l NaNO_3 or $\text{Na}_2\text{B}_4\text{O}_7$.

12. Process according to Claim 11, characterized by the dipping bath containing 30 g/l of NaOH and 40 g/l of NaNO_3 or $\text{Na}_2\text{B}_4\text{O}_7$.
13. Process according to one of the Claims from 3 to 7, characterized by being carried out with alternating voltage.
14. Process according to Claim 13, characterized by the dipping bath temperature being within the range from 35 to 45°C, and the current density (i) being within the range from 0.1 to 0.15 A/cm².
15. Process according to Claim 13 or 14, characterized by the dipping bath containing from 10 to 35 g/l NaOH and from 30 to 60 g/l NaNO_3 or $\text{Na}_2\text{B}_4\text{O}_7$.
16. Process according to Claim 15, characterized by the dipping bath containing from 25 to 35 g/l NaOH and from 40 to 50 g/l NaNO_3 or $\text{Na}_2\text{B}_4\text{O}_7$.
17. Process according to one of the Claims 13 to 16, characterized by the dipping bath containing from 10 to 15 g/l of NaOH and from 10 to 60 g/l of an alkali salt being selected from among the group comprising phosphates, acetates, carbonates, sulphates, oxalates, citrates, and borates of alkali metals.
18. Process according to one of the Claims from 1 to 17, characterized by the piece of material being subjected to a dipping treatment in an acid prior to anodic oxidation.

19. Process according to Claim 18, characterized by the use as an acid of H_2SO_4 of a minimum of 0.5 M, and the dipping treatment being carried out over a period of at least 10 seconds.
20. Process according to Claim 18, characterized by the use as an acid of H_2SO_4 of 2 M, and the piece of material being tempered after dipping treatment at approx. 200°C over a period of approx. 1 hour.
21. Process according to one of the Claims from 1 to 20, characterized by the piece of material being subjected to dipping treatment in an acid after anodic oxidation.
22. Process according to Claim 21, characterized by the use of 10% percentage CH_3COOH as an acid, and the dipping treatment being carried out for a minimum period of 30 seconds.
23. Process according to one of the Claims from 1 to 22, characterized by the surface layer being provided with a coating thickness of a minimum of $8\text{ }\mu\text{m}$.
24. Process according to one of the Claims from 1 to 23, characterized by the surface layer containing at least 50 % in weight of zinc.
25. A piece of material with a surface layer containing zinc, produced according to a method according to one of the Claims 1 to 24.
26. Process for the darkening of a surface layer made of ZnFe of a piece of material, during which the piece of material is subjected to a treatment in a dipping bath containing a hydrous solution of a hydroxide and a...

...nitrate, the hydrous solution having a pH value within the range from 9 to 14 and a NH_4NO_3 or NaNO_3 concentration within the range from 40 to 50 g/l, and the dipping bath being carried out at a temperature (T) within the range from 15 to 45°C.

27. Process according to Claim 26, characterized by the pH value of the bath exceeding 13, the bath temperature being within the range from 15 to 25°C, and the treatment period being minimum 10 seconds.
28. Process according to one of Claims 1 to 24, characterized by both of the electrodes for anodic oxidation being formed by a piece of material each whose surface layer contains zinc.

REVISED PAGE

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Dortmund, May 25, 2001

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IN THE UNITED STATES PATENT
AND TRADEMARK OFFICE

PATENT

Inventors:: Thomas Kruse, et al. Atty. Docket No. 27153.2400
Assignee: Ewald Dörken AG Client Ref. No.: 06918.1 Fsi/Sch
Serial No.: Filed:
Group Art Unit: Examiner:
Title: METHOD FOR DARKENING A SUPERFICIAL LAYER WHICH
CONTAINS ZINC AND WHICH IS OF A MATERIAL PIECE

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SNELL & WILMER LLP
One Arizona Center
400 East Van Buren
Phoenix, Arizona 85004-2202
Tel. (602) 382-6000
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By: 

Dr. Jochen Plaßmann, Managing Director

Dated: 5/6/01

SNELL & WILMER LLP
One Arizona Center
400 East Van Buren
Phoenix, AZ 85004-2202
TEL (602) 382-6337
FAX (602) 382-6070

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	First Named Inventor Thomas KRUSE	
	COMPLETE IF KNOWN	
	Application Number	/
	Filing Date	
	Group Art Unit	
	Examiner Name	To be assigned

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR DARKENING A SUPERFICIAL LAYER WHICH CONTAINS ZINC AND WHICH IS OF A MATERIAL PIECE

the specification of which (Title of the invention)

☐ is attached hereto
 OR

☒ was filed on (MM/DD/YYYY) 12/17/1999 as United States Application Number or PCT International

Application Number PCT/EP99/10036 and was amended on (MM/DD/YYYY) 11/15/2000 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?
198 58 795.3	Germany	12/18/1998	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>

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[Page 1 of 2]

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U.S. Parent Application or PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
PCT/EP99/10036	12/17/1999	

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Direct all correspondence to: ☒ Customer Number **020322** OR ☒ Correspondence address below

Name	Damon L. Boyd				
Address	SNELL & WILMER, LLP				
Address	One Arizona Center, 400 East Van Buren Street				
City	Phoenix	State	AZ	ZIP	85004-2202
Country	USA	Telephone	602-382-6337	Fax	602-382-6070

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Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle [if any])		Family Name or Surname			
Thomas		KRUSE			
Inventor's Signature	<i>Thomas Kruse</i>			Date	5/21/2001
Residence: City	Dortmund	State		Country	Germany
Post Office Address	Spissenagelstr. 94				
Post Office Address					
City	Dortmund	State		ZIP	44229
				Country	Germany

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DECLARATION

ADDITIONAL INVENTOR(S)

Supplemental Sheet

Page 1 of 1

Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle [if any])				Family Name or Surname			
Peter				MEISTERIAHN			
Inventor's Signature				Date		05/21/2001	
Residence: City		Iserlohn		State		Country Germany	
Post Office Address		Saatzweg, 70					
Post Office Address							
City		Iserlohn		State		Country Germany	
ZIP		58644		Country		Germany	
Name of Additional Joint Inventor, if any:							
<input type="checkbox"/> A petition has been filed for this unsigned inventor							
Given Name (first and middle [if any])				Family Name or Surname			
Inventor's Signature				Date			
Residence: City		State		Country		Citizenship	
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Name of Additional Joint Inventor, if any:							
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Inventor's Signature				Date			
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ZIP		58644		Country		Germany	
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Inventor's Signature				Date			
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